Specification

ROLLING BEARING

Technical Field

This invention relates to a rolling bearing and
particularly a rolling bearing which is used under such a condition
that water may seep in the lubricant or the bearing is affected by
high temperature, high-speed rotation or vibrations and is suitable
to electric parts and accessories of an automobile engine such as
an alternator.

Background Technique

A rolling bearing has a lubricant sealed in the annular
space formed by rolling elements and races thereby to protect the
rolling bearing from damage due to seizure and to prevent reduction
of bearing life L.

It is generally known that incorporation of water into the
lubricant results in great reduction in durability. For example,
incorporation of 6% of water into a lubricant reduces the rolling
fatigue life of the bearing to less than half to about one-twentieth
as reported in Kyozaburo Furumura, Shin-ichi Shirota and Kiyoshi
Hirakawa, *NSK Bearing Journal*, No. 636, pp. 1-10, "Hyomenkiten oyobi
naibukiten no korogarizukare ni tuite" (1977) (hereinafter referred
to as reference 1).

It is apparent from reference 1 that incorporation of water
into a lubricant is greatly influential on the life (durability)

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of a rolling bearing. Hence various techniques for preventing water's seeping into the lubricant of a rolling bearing have been studied and developed according to the use of the bearing.

Rolling bearings which are used under conditions that water may seep into the lubricant include those for a work roll of a rolling mill for iron and steel materials. Conventional bearings for the work roll have been protected against water's seeping into the lubricant of the bearing by fitting a contact rubber seal to the chock (a box for a bearing) in which the bearing is put so that a large amount of rolling water may be prevented from seeping into the chock. However, in case that the contact rubber seal undergoes deterioration or damage, water can seep into the chock and then into the lubricant of the bearing. Therefore it has recently been proposed to attach a contact rubber seal also to the inside of a bearing so as to avoid incorporation of water into the lubricant (see K. Yamamoto, M. Yamazaki, M. Akiyama, and K. Furumura, *Proceedings of the JSLE International Tribology Conference*, pp. 609-614, "Introducing of Sealed Bearings for Work Roll Necks in Rolling Mills", July 8-10, 1985, Tokyo, Japan (hereinafter referred to as a first prior art)).

According to the first prior art, a combined use of a contact rubber seal attached to the chock (outside a bearing) and a contact rubber seal attached to the inside of the bearing succeeds in reducing the water concentration in the lubricant from 40% to less than 10%, compared with use of only the contact rubber seal attached

to the chock for prevention of water incorporation. Further, the consumption of the lubricant can be diminished to 1/200. The report also mentions that the incidence of fracture accidents, which had been several times a year, was thereby reduced to zero.

There is another prior art for preventing water from seeping into the lubricant of the bearing for the above-described work roll, in which a lubricant is supplied to a chock together with compressed air as a carrier gas (see NSK Technical Journal No. 654, pp. 54-56 (1992), hereinafter referred to as a second prior art). According to the second prior art, the air pressure in the chock is set high by use of compressed air thereby making it possible to suppress water incorporation into the lubricant.

Other notable rolling bearings that might suffer from water incorporation into the lubricant are those for electric parts and accessories of an automobile engine. "Bearings for electric parts and accessories of an automobile engine" are those for ancillary parts driven by a belt outside an automobile engine, such as a bearing for an alternator, a bearing for an electromagnetic clutch of an air conditioner, a bearing for an idler pulley, and a bearing for a water pump. These electric part and accessory bearings are subject to invasion by muddy water or rain water splashed up from a road, and the water pump bearing is subject to invasion by circulating water for engine cooling.

From this viewpoint, techniques for enhancing the sealing performance of the inside seal have been suggested as a means for

preventing water's seeping into the lubricant of the bearings for electric parts and accessories of an automobile engine (see *NSK Technical Journal*, No. 660, pp. 15-22 (1995) and *ibid*, No. 652, pp. 66-67 (1992), hereinafter referred to a third prior art).

It has been reported that the durability of a rolling bearing generally reduces greatly where vibrations are applied or where the peripheries of a bearing have weak rigidity (see Yasuo Murakami and Hiromichi Takemura, *Preprints of Tribology Conference* held by Nippon Tribology Gakkai at Nagoya, Japan on Nov., 1993, pp. 295-298, "Densoyo jikuuke no flaking gensho no kenkyu", hereinafter referred to reference 2).

That is, where vibrations are applied during running, the oily film formed between raceways and rolling elements becomes insufficient to impose a tensile stress to the contact area, and where a rotating shaft and the inner race are fitted with a strong interference fit to reduce the rigidity of the bearing housing, a tensile stress always acts on the raceways. As a result, the bearing may tend to undergo early flaking under the influences of the water content originally present in the lubricant even with no water incorporated from the outside into the lubricant, resulting in a reduced bearing life L.

Now, the above-mentioned electric part and accessory bearings for an automobile engine directly receive the vibrations of the driving belt, and the bearing housing has low rigidity. Therefore, these bearings are very susceptible to the influences

of the vibrations and the like. In order to avoid early flaking due to vibrations, etc., use of grease acting like a vibration-damping buffer as a lubricant has been proposed (see *NSK Technical Journal*, No. 657, pp. 49-51 (1994), hereinafter referred to a fourth prior art).

Still other rolling bearings that might suffer from water incorporation into the lubricant are those for automobile wheels, guide rolls of iron and steel material continuous casting equipment, back-up rolls of a rolling mill, drier rolls of a paper machine, and so forth.

Bearings for automobile wheels are subject to invasion by water of muddy water or rain water on a road into their lubricant. Bearings for guide rolls of continuous casting equipment of iron and steel materials and those for back-up rolls of a rolling mill are also subject to invasion by cooling water or rolling water into the lubricant. Bearings for drier rolls of a paper machine are subject to attack of steam because they are used in a step of drying water-containing wet paper and are therefore liable to early fracture on account of the increased water content in the lubricant (see W.J. Culter, *TAPPI Journal*, Vol. 79, No. 2, pp. 157-167, "Paper Machine Bearing Failure" (1966), hereinafter referred to as reference 3)).

Hence, a combination of an outside contact rubber seal and an inside one as proposed in the first prior art or a high-performance seal has been adopted to bearings for automotive wheels (see *NSK*

Technical Journal, No. 647, pp. 55-57 (1987)), and a contact rubber seal has been applied to bearings for guide rolls or back-up rolls of a rolling mill in order to prevent invasion by water into the lubricant. A countermeasure against water incorporation should also be taken for bearings for a drier rolls of a paper machine because steam is liable to enter the bearing as is apparent from reference 3. However, since bearings for drier rolls of a paper machine are usually used under a high temperature condition, it is difficult to apply a contact rubber seal as used in the bearings for the work roll or the bearings for automotive wheels from considerations for heat resistance. Therefore, use of special rubbers for high temperatures which have sufficient heat resistance has been conceived for prevention of water penetration.

In short, the principle of using a contact rubber seal as suggested in the first prior art and the third prior art has been applied to the bearings for automobile wheels and other bearings to minimize water's seeping into the lubricant of the bearings (the prior art related to the other rolling bearings will hereinafter referred to a fifth prior art).

On the other hand, where a machine or automobile in which bearings are used is suspended, and the temperature in the bearing housing drops to the dew point, the moisture in the peripheries of the bearings condenses to water droplets, which adhere to the bearings or infiltrate into the lubricant to cause reduction of the bearing life L as reported in Ken-ichi Uchida, *NSK Technical Journal*,

No. 632, pp. 40-45 (1973), hereinafter referred to as reference 4.

It is also reported that deterioration of a lubricant by oxidation is accompanied by water generation, and the generated water adheres to the bearing to give rise to reduction of the bearing life L (see Masao Seki, *Preprints of Symposium on Rolling Fatigue*, pp. 125-130 (1993), hereinafter referred to as reference 5).

According to references 4 and 5, cases are met with in which a lubricant can contain water with environmental changes and the like even though water does not seep in directly from the outside. Therefore, it is necessary to consider some counter means other than the above-described contact rubber seal against water infiltration into the lubricant in order to avoid reduction of the bearing life L.

From this standpoint, use of martensitic stainless steel (SUS 440C) as a bearing material to be used for bearings has been suggested to protect bearings from rust due to water adhesion thereby preventing durability reduction (see Korogari Jikuuke Kogaku Hensyu Iinkai (ed.), *Korogari Jikuuke Kogaku*, pp. 71-72, Yokendo (1976), hereinafter referred to as a sixth prior art).

As mentioned above, the first prior art made it possible to decrease the water concentration in a lubricant from 40% to less than 10% and to reduce the consumption of the lubricant. A later survey of actual use of work roll bearings found that seizure accidents reduced drastically, but it turned out that the time until flaking, i.e., the bearing life L was not so improved. It seems

that the reduction of seizure accidents is attributed to reduction of leakage of the lubricant by the contact rubber seal fitted in the inside of the bearings and that the failure to improve the bearing life L is because water seeps in the lubricant to greatly reduce the rolling fatigue strength of the bearing.

A report says that incorporation of as little as about 100 ppm of water into a lubricant can cause a reduction in rolling fatigue strength by 32 to 48% (see P. Schatzberg and I.M. Felsen, Wear, Vol. 12, pp. 331-342, "Effects of water and oxygen during rolling contact lubrication" (1968), hereinafter referred to as reference 6)). With a contact rubber seal fitted to the chock outside a bearing combined with a contact rubber seal fitted inside the bearing, the water concentration in the lubricant can be controlled below about 10%, but water cannot be completely prevented from seeping into the lubricant so that the rolling fatigue strength of the bearing material unavoidably reduces as pointed out in reference 6. That is, the first prior art fails to completely prevent water from seeping into the lubricant. The rolling fatigue strength of the bearing material reduces as a result, failing to secure durability with a desired bearing life L.

The second prior art, which prevents water's seeing by increasing the air pressure in the chock, does not rely on the waterproofing ability of a contact rubber seal as in the first prior art. The problem of the second prior art, however, lies in the difficulty in achieving prevention of water's seeping to such an

almost perfect degree that the water concentration in the lubricant be kept at 100 ppm or lower.

The third prior art is in principle similar to the first prior art in that water is prevented from seeping by means of a contact rubber seal. Accordingly, it meets difficulty in controlling the water concentration in the lubricant at or below 100 ppm as stated above, thus failing to obtain desired durability.

Because of the recent advancement of automobile performance, the working temperature of the bearings of electric parts and accessaries has been elevating. It follows that the grease according to the fourth prior art softens to reduce its vibration damping capacity, resulting in a failure to prevent early flaking of the bearing. The early flaking combined with water incorporated into the lubricant can cause reduction in bearing life, failing to obtain desired durability.

In recent years, the spread of front engine front drive cars aiming at size and weight reduction, the demand for widening car space, and the like have put us under the pressing necessity of narrowing the engine room space. This also necessitates promoting size and weight reduction of ancillary engine parts mounted on automobiles, such as an alternator. And yet, on the other hand, there is a demand for these ancillary engine parts to have higher performance and higher output. Size reduction of ancillary engine parts is unavoidably accompanied with a reduction in output. The reduction in output of, for example, an alternator or an

electromagnetic clutch of an air conditioner is compensated for by speeding up, and an idler pulley has increased its speed accordingly.

In order to abate the engine noise, closure of the engine room is also requested. As the closure of the engine room is getting tighter, the inner temperature of the engine room increases. As a result, the working temperature of the bearings for the electric parts and accessaries increases. Further, the increased tension of the driving belt has been increasing the load on the bearings. Thus the conditions of use of rolling bearings in the ancillary engine parts have been getting more and more rigid.

In cases where bearings for electric parts and accessaries are used under such high temperature and high speed conditions, softening of grease is accelerated to reduce seizure resistance of the grease, and the damping capacity of the grease also decreases to incur early flaking of the bearings, resulting in a failure to obtain desired durability.

The fifth prior art is in principle similar to the first prior art in respect of use of a contact rubber seal and therefore has the difficulty in perfectly preventing water's seeping.

The sixth prior art involves the following problem. Stainless steel has lower heat conductivity than low alloy steel and is therefore more liable to seizure fracture. Therefore, it is difficult to apply stainless steel to those bearings which are used under the above-described poor lubricating conditions that may allow water to enter the lubricant. Anticorrosion of the stainless

steel is maintained by the passivation film formed on the surface. In a rolling bearing, however, the passivation film is broken on contact between the track surface of the races and the rolling surface. As a result, corrosion proceeds selectively to form pits, from which flaking fracture is apt to initiate. Furthermore, since stainless steel is hardened at a high temperature from 1010 to 1070°C in the production of bearings, a salt bath furnace should be used as a heating furnace, which may incur an increase of cost of production facilities (see Nihon Tekko Kyokai (ed.), *Ko no netsushori, 5th Ed.*, pp. 563-586 (1989)).

Additionally the grinding speed of stainless steel is lower on account of the lower heat conductivity as described above, which increases the grinding cost. The stainless steel itself, being high alloy steel, increases the material cost.

The present invention has been made in the light of the above-described problems. An object of the invention is to provide a rolling bearing which secures a sufficient bearing life easily and economically even when used under such conditions that outside water or water of moisture condensation may seep in the lubricant or the bearing is influenced by vibrations.

Disclosure of the Invention

The applicant of the invention has extensively studied in order to obtain a rolling bearing which is protected against propagation of corrosion at the bearing site even when used under lubricating conditions with the lubricant containing water. As a

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result, he has found it important to control the cathode reaction on the raceway of the races so as to inhibit hydrogen from being absorbed in the races. He has also found it effective for this purpose to drop the hydrogen ion concentration in the lubricant, which is in other words to raise the hydrogen ion exponent pH of the lubricant.

The applicant's experiment in which an alkaline substance is added to a lubricant in increasing amounts revealed that the cathode reaction can be suppressed to improve the rolling fatigue strength when the hydrogen ion exponent pH of the lubricant is in the range of from 7 to 13.

The present invention has been reached based on these findings. The rolling bearing according to the invention has outer and inner races and rolling elements which are rotatably put in between the outer and inner races with a lubricant sealed into the annular space formed by the rolling elements and the races, and is firstly characterized in that the hydrogen ion exponent pH of the lubricant is in the range of from 7 to 13.

It is known that an organic metal salt in a lubricant forms a chemical reaction film on the steel surface of a bearing material, which prevents metal-to-metal contact and reduces the coefficient of friction, bringing about improvements in load resistance, seizure resistance, and wear resistance.

Noting such a function of an organic metal salt, the applicant has further studied extensively and found, as a result,

that early flaking of a bearing can be prevented by setting the hydrogen ion exponent pH of a lubricant at 5 or higher where the lubricant contains an organic metal salt. It has also proved that the same effect can be produced when an ash-free dialkyldithiocarbamic acid (ADTC) is added to the lubricant in place of the organic metal salt.

Thus, the rolling bearing according to the invention is secondly characterized in that the lubricant contains an organic metal salt or ADTC and has its hydrogen ion exponent pH adjusted in a range of from 5 to 13.

In addition to the above-mentioned approach relying on cathode reaction control, it is also considered effective for preventing corrosion progress in the bearing site to minimize small crevices that may be formed between non-metallic inclusions and the metal matrix on the bearing material.

Improvement on oily film formation between the rolling surface and the raceway surface is believed to reduce the tangential force between the rolling surface and the raceway surface thereby to suppress formation of such small crevices.

Paying attention to this respect, the applicant continued his study and has found that a sufficiently strong oily film can be formed between the rolling surface and the raceway surface by incorporating fine particles of an inorganic compound having an average particle size of 2 μm or smaller into the lubricant and by adjusting the hydrogen ion exponent pH of the lubricant at 5 or higher,

whereby the metal-to-metal contact can be prevented to improve the bearing life L under high temperature and high speed conditions.

Hence, the rolling bearing according to the invention is thirdly characterized in that the lubricant contains an inorganic compound having an average particle size of 2 μm or smaller and has a hydrogen ion exponent pH adjusted in a range of from 5 to 13.

Further, the results of the applicant's study have revealed that a sufficiently strong oily film is similarly formed between the rolling surface and the raceway surface when a diurea compound containing an aromatic amine or a mixture of two or more kinds of the diurea compound is added to the lubricant as a thickener in place of the inorganic compound.

Accordingly, the rolling bearing according to the invention is fourthly characterized in that the lubricant contains as a thickener a diurea compound containing an aromatic amine or a mixture of two or more kinds of the diurea compound and has a hydrogen ion exponent pH adjusted in a range of from 5 to 13.

In addition, the object of the present invention can be accomplished by not only the rolling bearing having any one of the above-mentioned 1st to 4th characteristics but an appropriate combination of the 1st to 4th characteristics.

Brief Description of the Drawings

Fig. 1 is a characteristic diagram showing the relationship of amount of TeDTC added vs. flaking life in 2nd Example.

Fig. 2 is a characteristic diagram showing the relationship

of hydrogen ion exponent pH vs. flaking life in 2nd Example.

Fig. 3 is a characteristic diagram showing the relationship of amount of diurea compound added vs. aromatic ring molar ratio Z in 4th Example.

Best Mode for Carrying out the Invention

The modes in the practice for carrying out the invention will be described below.

[First Mode]

A rolling bearing is generally used with a lubricant sealed into the annular space formed between rolling elements and races. Although it is known, as previously described, that the state of the lubricant's containing water causes reduction of rolling fatigue strength of the bearing material, there is no established theory about this phenomenon. That is, the mechanism accounting for the reduction of rolling fatigue strength by incorporation of water into a lubricant remains unknown (see E. Ioannides and B. Jacobson, *Ball Bearing Journal Special '89*, pp. 22-27, "Dirty lubricants-reduced bearing life" (1989)).

First of all the applicant set about elucidating the mechanism in question theoretically.

Where water enters a lubricant, even a trace amount of water can make oily film formation difficult, and rolling elements and races undergo metal-to-metal contact between the rolling surface and the raceway surface. The surfaces of the rolling elements and races are not homogeneous, and non-metallic inclusions such as

oxides and sulfides are unavoidably formed on the rolling surface or raceway surface. If the lubricant contains water, water penetrates into the interface between the non-metallic inclusions and the metal matrix mainly comprising Fe and forms local-action-cells to develop local corrosion. Since there is always a rolling element/race contact area in the vicinities of the above-described interface, a tensile stress is of necessity imposed on the interface between the non-metallic inclusion present on the raceways or rolling surface and the metal matrix. Under such a tensile stress imposed, there is formed a small crevice in the interface between the non-metallic inclusion and the metal matrix. Where water is present in the lubricant, however slight the water content may be, the water preferentially enters the small crevice through capillarity because of its lower viscosity than the lubricant. This cause corrosion reaction to occur in that small crevice. Moreover, where a rotating shaft is fitted into the inner race with an interference fit, a tensile stress is always imposed on the raceway so that a greater tensile stress will be loaded on the interface between the non-metallic inclusion and the metal matrix. In this case, the crevices will be formed under the greater tensile stress.

In a rolling bearing used in electric parts and accessaries of automobile engine, such as an alternator, vibrations of a driving belt are directly transmitted to the bearing, and the bearing housing has low rigidity. Therefore metal-to-metal contact occurs
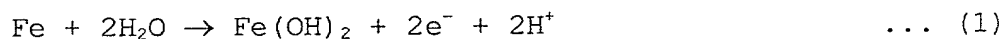
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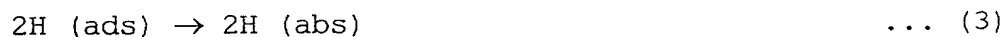frequently between the raceway surface of races and the rolling surface of the rolling elements in spite of the high speed of rotation. It follows that the tightness between the non-metallic inclusion and the metal matrix on the raceway surface and rolling surface diminishes to form small crevices in their interface. The water content in the lubricant tends to enter these small crevices to cause corrosion reaction. Corrosion of this kind is apt to develop particularly on the raceway surface of the outer race. The lubricant usually has some water content attributed to moisture absorption from the air. The water content originally present in the lubricant may induce corrosion reaction even if outside water does not seep in.

The corrosion reaction product clogs the inlets to the crevices so that oxygen is hardly supplied from the surface to the crevices. Then, the metal matrix in the deepest part of the crevices acts as an anode, while carbides and the metal matrix of the area other than the deepest area serve as a cathode, to cause corrosion reactions involving hydrogen evolution as represented by chemical reaction formulae (1) through (4):

Anode Reaction:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + 2e^- + 2H^+ \qquad \ldots (1)$$

Cathode Reaction:

$$2H^+ + 2e^- \rightarrow 2H \ (ads) \qquad \ldots (2)$$

$$2H \ (ads) \rightarrow 2H \ (abs) \qquad \ldots (3)$$

$$2H \ (abs) \rightarrow H_2\uparrow \qquad \ldots (4)$$

wherein H (ads) means a hydrogen atom adsorbed onto the surface of a bearing material; and H (abs) means a hydrogen atom absorbed into the inside of the bearing material.

On the anode side, Fe reacts with water to undergo oxidation to release an electron as shown in chemical reaction formula (1). On the cathode side, hydrogen is adsorbed onto the surface of the bearing material as shown by chemical formula (2) because of oxygen starvation in the inside of the small crevices. Then a part of the adsorbed hydrogen diffuses in the inside of the bearing material and absorbed as shown by chemical reaction formula (3). The rest of the adsorbed hydrogen on the surface of the bearing material gathers together to form hydrogen molecules (gas), which are released outside. On the carbides as a cathode, the chemical reaction represented by formula (4) takes place primarily while progress of the reaction of formula (3) is practically negligible. However, on the metal matrix acting as a cathode, both the reactions of formulae (3) and (4) proceed.

Accordingly, in case of water's penetration into the crevices during running of a bearing, no matter how slight it may be, the bearing material absorbs hydrogen. The bearing material thus undergoes hydrogen embrittlement and reduces its rolling fatigue strength, which causes flaking and reduction of the bearing life L.

From this point of view it is necessary to control hydrogen absorption into the inside of the bearing material thereby to avert

hydrogen embrittlement. It is important for this purpose to control the cathode reaction of chemical reaction formula (2) in the light of the above-described corrosion reaction mechanism. In order to control the cathode reaction of chemical reaction formula (2), it is required to decrease the hydrogen ion concentration of the lubricant. In other words, the reaction rate of the chemical reaction formula (2) can be lowered by raising the hydrogen ion exponent pH of the lubricant. To this effect the hydrogen ion exponent pH should be limited within a range of from 7 to 13.

The hydrogen ion exponent pH of the lubricant and the composition of the lubricant (base oils, thickeners, and pH adjustors) according to this mode will be described.

[Hydrogen ion exponent pH of Lubricant and Composition of Lubricant]

(1) Hydrogen ion exponent pH

The water content often shows acidity, having a hydrogen ion exponent of 7 or less, due to dissolution of carbon dioxide which is present in the atmosphere in a trace amount. The hydrogen ion exponent pH of a lubricant can be increased by addition of an alkaline substance as a pH adjustor. In order to diminish the reaction rate of the chemical reaction formula (2) to sufficiently suppress hydrogen absorption in the race material thereby to extend a bearing life L, it is necessary to adjust the hydrogen ion exponent pH to 7 or higher. If the hydrogen ion exponent pH exceeds 13 on the other hand, caustic corrosion develops to wear the raceway surface and rolling surface, and vibrations during running of the bearing

gradually becomes noticeable. Accordingly, the hydrogen ion exponent pH of the lubricant according is limited to 7 to 13 in this mode.

(2) Base Oil

Base oils serving for lubrication are not particularly limited. Any of oils that are commonly used as a base oil of lubricating oils is useful. It is desirable to use base oils having a dynamic viscosity of 40 to 400 mm^2/sec, preferably 60 to 250 mm^2/sec, at 40°C in order to avoid abnormalities at the start in low temperature that might occur in case of shortage of low temperature flowability or to form a still stronger oily film for enhancing seizure resistance.

Useful base oils include mineral lubricating oils, synthetic lubricating oils, and natural lubricating oils.

The mineral lubricating oils include those obtained by an appropriate combination of purification techniques, such as vacuum distillation, solvent deasphalting, solvent extraction, hydrogenolysis, solvent dewaxing, sulfuric acid treatment, clay treatment, hydrorefining, and the like.

The synthetic lubricating oils include hydrocarbon oils, aromatic oils, ester oils, and ether oils.

The hydrocarbon oils include normal paraffins, isoparaffins, and poly-α-olefins (PAO), such as polybutene, polyisobutylene, 1-decene oligomers, 1-decene, and ethylene oligomers, and hydrogenation products thereof.

The aromatic oils include alkylbenzenes such as monoalkylbenzenes and dialkylbenzenes, and alkylnaphthalenes such as monoalkylnaphthalenes, dialkylnaphthalenes, and polyalkylnaphthalenes.

The ester oils include diester oils such as dibutyl sebacate, di-2-ethylhexyl sebacate, dioctyl adipate, diisodecyl adipate, ditridecyl adipate, ditridecyl glutarate, and methylacetyl ricinoleate; aromatic ester oils such as trioctyl trimellitate, tridecyl trimellitate, and tetraoctyl pyromellitate; polyol ester oils such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate, and pentaerythritol pelargonate; and complex ester oils, which are oligoesters between polyhydric alcohols and dibasic-monobasic mixed fatty acids.

The ether oils include polyglycols such as polyethylene glycol, polypropylene glycol, polyethylene glycol monoethers, and polypropylene glycol monoethers; and phenyl ether oils such as monoalkyltriphenyl ethers, alkyldiphenyl ethers, dialkyldiphenyl ethers (DAPE), pentaphenyl ether, tetraphenyl ether, monoalkyltetraphenyl ethers, and dialkyltetraphenyl ethers.

Other synthetic lubricating oils, such as tricresyl phosphate, silicone oils and perfluoroalkyl ethers, are also useful.

The above-enumerated lubricating oils can be used individually as a base oil, or a mixture prepared by mixing two or

more of these lubricating oils to have a desired dynamic viscosity

can also be used as a base oil.

(3) Thickener

A thickener is incorporated into the lubricant to keep the

lubricant in a semi-solid state and to improve the properties of

the oil (viscosity, elasticity, plasticity, etc.). The thickener

is made up of molecules or crystals linked in chain into fibers,

which are dispersed in the base oil to form a gel structure.

Therefore, the thickener is not particularly limited as

long as it has an ability of holding the base oil in the gel structure.

It is possible to use a thickener appropriately selected from among,

for example, metal soaps comprising Li, Na, etc., complex metal soaps

comprising Li, Na, Ba, Ca, etc., and urea compounds such as diurea

compounds and polyurea compounds.

From the standpoint of obtaining improved heat resistance

of the lubricant, it is preferred to use diurea compounds capable

of forming a firm gel structure. The diurea compounds are compounds

obtained by reacting a diisocyanate and a monoamine under

predetermined conditions, which are represented by formula (1):

$$R^1 - NH\overset{\overset{\textstyle O}{\|}}{C}NH - R^2 - NH\overset{\overset{\textstyle O}{\|}}{C}NH - R^3 \qquad (1)$$
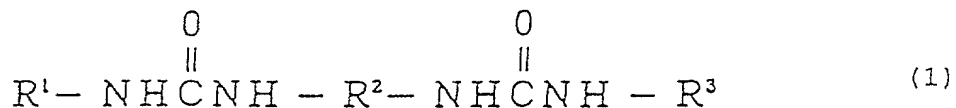
wherein R^1 and R^3 each represent an amine residue made up of, e.g.,

a cyclohexyl group, a C_n alkylcyclohexyl group (n=7 to 12) or a C_n

straight-chain alkyl group (n=8 to 20); and R^2 represents an

isocyanate residue made up of a divalent aromatic ring-containing C_n hydrocarbon group (n=6 to 15).

(4) pH Adjustor

A pH adjustor is added to adjust the hydrogen ion exponent pH of the lubricant within a range of from 7 to 13. As described above, because the water content has dissolved therein carbon dioxide that is present in the atmosphere in a trace amount, the lubricant often becomes acidic having a hydrogen ion exponent pH of 7 or lower. Therefore, it is necessary to add an alkaline substance as a pH adjustor so as to adjust the hydrogen ion exponent pH to 7 to 13. At least one alkaline substance selected from amine compounds, organic metal salts, organic acid metal salts, and alkaline inorganic compounds can be used.

The amine compound can be any of the primary to tertiary amines represented by respective formulae (2) to (4):

$$R^4 - NH \tag{2}$$

$$\frac{R^4}{R^5} > NH \tag{3}$$

$$\frac{R^4}{R^5} > N - R^6 \tag{4}$$
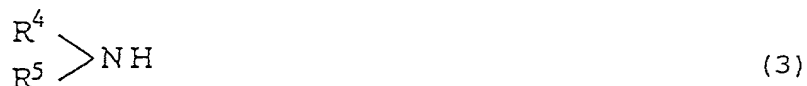
wherein R^4, R^5, and R^6, which may be the same or different, are each selected appropriately from an aliphatic hydrocarbon group, an alicyclic hydrocarbon group and an aromatic hydrocarbon group,

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which each has carbon atoms C_n (n=1 to 24), and a derivative thereof.

The aliphatic hydrocarbon group includes a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, an octyl group, a dodecyl group, a tetradodecyl group, an octadecyl group, and an eicosyl group.

The alicyclic hydrocarbon group typically includes a cyclohexyl group.

The aromatic hydrocarbon group includes a phenyl group, a methylphenyl group, and an ethylphenyl group.

The derivatives of these groups include a polyoxyalkylene group, a polyoxyethylene group, and a polyoxyethylene group.

The organic metal salts or organic acid metal salts which can be used include those composed of a C_n (n=6 to 24) hydrocarbon chain constituting an alkyl group and a metallic element, which constitutes the metal salt, selected from alkali metals (Na, K, Li, etc.), alkaline earth metals (Mg, Ca, Ba, etc.), Al, Zn, etc. and mixtures of two or more thereof.

The alkaline inorganic compounds which can be used include metal hydroxides such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and aluminum hydroxide (Al(OH)$_3$); metal carbonates such as sodium carbonate (Na$_2$CO$_3$), potassium carbonate (K$_2$CO$_3$), lithium carbonate (Li$_2$CO$_3$), and sodium hydrogencarbonate (NaHCO$_3$); metal borates such as sodium borate (Na$_3$BO$_3$) and lithium borate (Li$_3$BO$_3$); and metal silicates such as sodium silicate (Na$_4$SiO$_4$) and potassium silicate (K$_4$SiO$_4$).

(5) Other Additives

If desired, it is a preferred practice to add to the lubricant various additives, such as gelling agents, antioxidants, extreme pressure agents, oiliness. improvers, rust inhibitors, metal-inactivating agents, viscosity index improvers, and so forth, in order to further improve the lubricant performance.

The gelling agents include metal soaps, Benton, and silica gel. The antioxidants include amine compounds, phenol compounds, sulfur compounds, and zinc thiophosphate. The extreme pressure agents include chlorine compounds, sulfur compounds, phosphorus compounds, zinc dithiophosphate, and organomolybdenum compounds. The oiliness improvers include fatty acids and animal and vegetable oils. The rust inhibitors include petroleum sulfonate, dinonylnaphthalene sulfonate, and sorbitan esters. The metal-inactivating agents include benzotriazole and sodium nitrite. The viscosity index improvers include polymethacrylates, polyisobutylene, and polystyrene.

These additives can be used either individually or as a combination of two or more thereof. While not particularly limiting, the additives are added to give an additive content of not more than 20% by weight in the lubricant.

The applicant then investigated the flaking characteristics of various bearing sites in case where water has seeped into the lubricant.

As previously stated, if water enters the lubricant, the

time required for a rolling bearing to flake, namely, the bearing life L is shortened. In general it is the fixed race that undergoes flaking most frequently of the bearing constituting sites, and the frequency of flaking decreases in the order of the rotating race and the rolling elements. The lower frequency of flaking on the rolling elements than the frequency of flaking on races is ascribable to a smaller hydrogen absorption by the rolling elements than those by the races. The following reasons could account for this.

(1)   In a rolling bearing, the rotation speed of the rolling elements is generally far higher than that of races. Therefore, even though small crevices are formed on the rolling surface of the rolling elements, the water entering the crevices is expelled by centrifugal force. As a result, propagation of corrosion reaction is suppressed, and the amount of hydrogen absorbed and penetrating deep into the inside of the material is reduced.

(2)   The working ratio of a cast material (an ingot, a bloom, a billet, etc.) into rolling elements is higher than that into races so that the non-metallic inclusion present on the rolling surface of the rolling elements is smaller than that present on the raceway surface of the races. In the rolling elements, the interface between the non-metallic inclusion and the metal matrix is therefore smaller and shallower. As a result, the progress of corrosion reaction of hydrogen evolution type is suppressed, and the hydrogen absorption inside the material is lessened.

As for the races, the following reason could be furnished

for the lower frequency of flaking on the rotating race than on the fixed race. In general, if water enters the small crevices formed on the surface of the rotating race, it is apt to be expelled to reduce the hydrogen absorption as compared with the fixed race. The frequency of flaking thus seems to be decreased. However, where the inner race and the rotating shaft are an interference fit, a tensile stress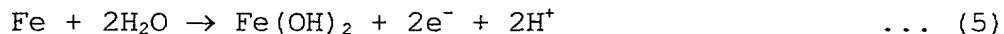 is always exerted on the raceway of the rotating race. In this case, even through the inner race is a rotating race, stress corrosion is accelerated, and the chemical reaction represented by the above-described reaction formula (2) proceeds apace to increase the hydrogen absorption of the rotating race, resulting in an increased flaking frequency. In particular where the interference exceeds 7/10000 of the rotating shaft diameter or where a bearing having a tapered bore is used with an interference fit, the incidence of flaking of the rotating race is equal to or higher than that of the fixed race. In cases where the inner race is a fixed race, and the inner race and a rotating shaft are fitted with an interference fit, it is needless to say that the hydrogen absorption increases as compared with the cases of a clearance fit.

Attention here paid to the metal-to-metal contact between the rolling surface of the rolling elements and the raceway surface of the races, it is effective to change localized corrosion to contact corrosion, with the metal matrix side inside the crevice formed in the metal matrix/non-metallic compound interface taken as an anode, and the metal matrix on the rolling surface of the

rolling elements as a cathode.

The metal matrix existing on the rolling surface of the rolling elements (hereinafter referred to as a rolling surface metal matrix) is made electrochemically noble over the metal matrix existing on the raceway surface of the races (hereinafter referred to as a race metal matrix), whereby the metal matrix side in the crevice serves as an anode, and the metal matrix on the rolling surface as a cathode. Thus, the anode reaction takes place on the metal matrix side on the interface, while the cathode reaction occurs on the rolling surface metal matrix. Since the rolling surface is easily provided with oxygen from the surroundings, the corrosion mode becomes oxygen-consuming corrosion reaction as represented by chemical reaction formulae (5) and (6) shown below. Hydrogen absorption inside the races is thus controlled, and a reduction in bearing life due to hydrogen embrittlement can be averted. In this case, too, carbides in the crevice still work as a cathode, but the reaction of chemical reaction formula (3) which causes hydrogen embrittlement hardly proceeds on the carbides. It is the reaction of chemical reaction formula (4) that chiefly proceeds on the carbides. Therefore hydrogen absorption inside the races does not occur.

Anode Reaction:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + 2e^- + 2H^+ \qquad \ldots (5)$$

Cathode Reaction:

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad \ldots (6)$$

A metallic matrix that becomes electrochemically noble can be obtained at low cost by increasing the retained austenite concentration in the bearing material having been subjected to full hardening and tempering. The following methods are applied for increasing the retained austenite concentration.

[Method for Increasing Retained Austenite Concentration]

(1) Adjusting the temperature at which austenite starts martensitic transformation (Ms point).

An Ms point is decided by the chemical components of material steel, the concentration of surface carbon or nitrogen added by carburizing or carbonitriding, the metallurgical structure before hardening, the hardening temperature, the hardening time, and so forth. For example, the higher the Mn content of material steel, the higher the retained austenite concentration. Where the material steel has been carburized prior to hardening, the higher has the retained austenite concentration been increased, the higher the retained austenite concentration. The smaller the carbide particle size, or the higher the hardening temperature, or the longer the retention time of hardening, the higher the retained austenite concentration.

(2) Adjusting the cooling rate in hardening.

The lower the cooling rate in hardening, the higher the retained austenite concentration.

(3) Adjusting the tempering conditions.

The lower the tempering temperature or the shorter the

heating temperature in tempering, the higher the retained austenite concentration.

(4) Controlling the conditions for carrying out subzero treatment.

The higher the temperature of subzero treatment (cooling to temperature below room temperature), or the shorter the subzero treating time, the higher the retained austenite concentration. Not carrying out subzero treatment brings about a higher retained austenite concentration.

(5) Not carrying out work hardening such as shot peening.

Where shot peening is not carried out, the retained austenite concentration is higher than the case where conducted.

It is not only technically difficult but economically disadvantageous to control corrosion reaction by using such high alloy steel as stainless steel (SUS 440C) as a bearing material as previously mentioned. It is preferred to use low alloy steel as material steel for bearings. For example, it is effective to use low alloy steel comprising 0.10 to 1.10 wt% of C, 0.75 wt% or less of Si, 1.70 wt% or less of Mn, 1.80 wt% or less of Cr, 1.50 wt% or less of Mo, 4.50 wt% or less of Ni, 0.30 wt% or less of Cu, 0.050 wt% or less of Al, and the balance of Fe and unavoidable impurities (O, S, Ti, etc.) as material steel for various parts of a bearing and to carry out desired heat treatment on the material steel to obtain bearing parts having desired surface hardness.

Because corrosion reaction on the races initiates from the small crevices formed between the non-metallic inclusions and the

metal matrix, it is also preferred for corrosion prevention to suppress formation of non-metallic inclusions. For this purpose it is desirable that the oxygen content, the sulfur content, and the titanium content, which lead to formation of oxides, sulfides or titanium compounds constituting the non-metallic inclusions, be reduced to 9 ppm or less, 50 ppm or less, and 40 ppm or less, respectively. In order to obtain satisfactory intimate contact between the non-metallic inclusions and the metal matrix thereby averting formation of the small crevices in that interface, it is desirable that the final refining of the bearing material be performed by an ESR process or a VAR process.

[Second Mode]

In the above-described first mode, the hydrogen ion exponent pH is adjusted within a range of 7 to 13 to suppress hydrogen absorption in the inside of a bearing material to avoid hydrogen embrittlement, thereby averting reduction in bearing life L. According to the second mode of the invention, an organic metal salt or an ash-free dialkyldithiocarbamic acid (ADTC) is incorporated into the lubricant to form a firm reaction film in the small crevices formed between non-metallic inclusions and the metal matrix, whereby a rolling bearing having a desired bearing life L can be obtained only if the hydrogen ion exponent pH is higher than or equal to 5 even though it is 7 or lower.

The base oils, thickeners and pH adjustors used in the lubricant are the same as those in the first mode. In what follows,

the reaction film forming agent (i.e., organic metal salt or ADTC) and the hydrogen ion exponent pH that characterize the second mode will be explained.

(1) Reaction Film Forming Agent

The action and effect observed in the use of an organic metal salt as a reaction film forming agent are described below.

An organic metal salt has conventionally been used in lubricants as such an additive as an extreme pressure agent or part of an antioxidant. A lubricant containing an organic metal salt forms a chemical reaction film on the surface of a steel bearing material. That is, the presence of an organic metal salt in the lubricant provides a firm reaction film composed of the organic metal salt in the small crevices formed between non-metallic inclusions present on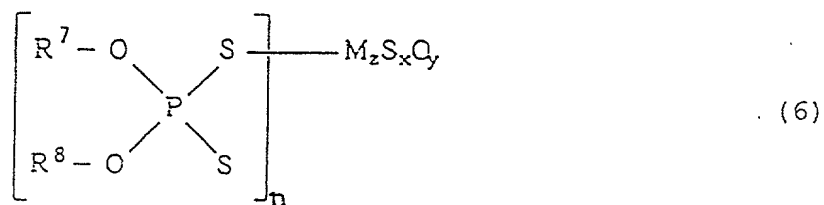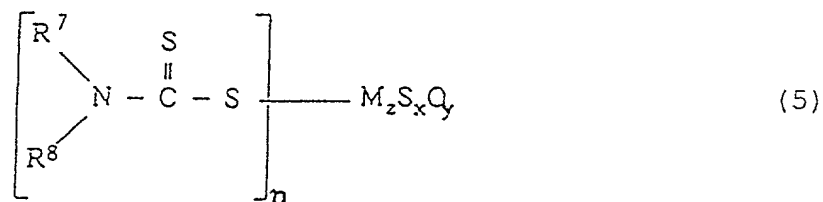 the surface of the bearing material and the metal matrix. A metal-to-metal contact is thereby prevented, and the coefficient of friction reduces to obtain improvements in load resistance, seizure resistance, and wear resistance.

Further, where a specific organic metal salt is incorporated into the lubricant, and the above-described firm reaction film is formed in the small crevices before corrosion reaction of hydrogen evolution type takes place, the progress of the cathode reaction represented by chemical reaction formula (2) is restrained, or hydrogen atoms adsorbed onto the surface of the bearing material is prevented from diffusing into the inside of the bearing material. As a result, the early flaking of the bearing

material is avoided thereby to improve the bearing life L.

Organic metal salts which produce such an action and an effect include dialkyldithiocarbamic acid (DTC) compounds represented by formula (5) and dialkyldithiophosphoric acid (DTP) compounds represented by formula (6):
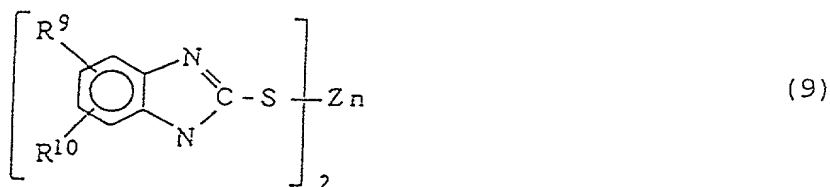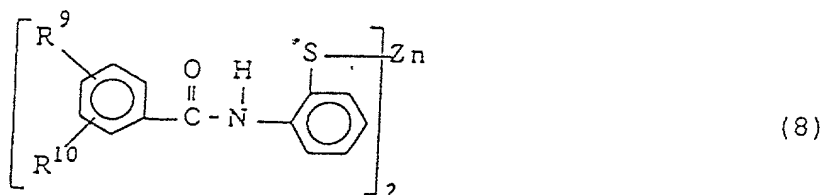
$$\left[\begin{array}{c} R^7 \\ \\ N - \overset{\overset{\displaystyle S}{\|}}{C} - S \\ \\ R^8 \end{array} \right]_n \!\!\!\!\! - M_z S_x O_y \qquad (5)$$

$$\left[\begin{array}{c} R^7 - O \\ \\ P \\ \\ R^8 - O \end{array} \begin{array}{c} S \\ \\ \\ S \end{array} \right]_n \!\!\!\!\! - M_z S_x O_y \qquad (6)$$

wherein n is 2, 3 or 4; x, y, and z is 0, 1, 2, 3 or 4; M represents a metal species, specifically Sb, Bi, Sn, Ni, Te, Se, Fe, Cu, Mo or Zn; R^7 and R^8, which may be the same or different, each represent an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, an alkylaryl group or an arylalkyl group.

Particularly preferred groups as R^7 and R^8 include a 1,1,3,3-tetramethylbutyl group, a 1,1,3,3-tetramethylhexyl group, a 1,1,3-trimethylhexyl group, a 1,3-dimethylbutyl group, a 1-methylundecane group, a 1-methylhexyl group, a 1-methylpentyl group, a 2-ethylbutyl group, a 2-ethylhexyl group, a 2-methylcyclohexyl

group, a 3-heptyl group, a 4-methylcyclohexyl group, an n-butyl group, an isobutyl group, an isopropyl group, an isoheptyl group, an isopentyl group, an undecyl group, an eicosyl group, an ethyl group, an octadecyl group, an octyl group, a cyclooctyl group, a cyclododecyl group, a cyclopentyl group, a dimethylcyclohexyl group, a decyl group, a tetradecyl group, a docosyl group, dodecyl group, a tridecyl group, a trimethylcyclohexyl group, a nonyl group, a propyl group, a hexadecyl group, a hexyl group, a heneicosyl group, a heptadecyl group, a heptyl group, a pentadecyl group, a pentyl group, a methyl group, a t-butylcyclohexyl group, a t-butyl group, a 2-hexenyl group, a 2-methallyl group, an allyl group, an undecenyl group, an oleyl group, a decenyl group, a vinyl group, a butenyl group, a hexenyl group, a heptadecenyl group, a tolyl group, an ethylphenyl group, an isopropylphenyl group, a t-butylphenyl group, a sec-pentylphenyl group, an n-hexylphenyl group, a t-octylphenyl group, an isononylphenyl group, an n-dodecylphenyl group, a phenyl group, a benzyl group, a 1-phenylethyl group, a 2-phenylethyl group, a 3-phenylpropyl group, a 1,1-dimethylbenzyl group, a 2-phenylisopropyl group, a 3-phenylhexyl group, a benzhydryl group, and a biphenyl group. These groups may contain an ether linkage.

Further, organozinc compounds represented by formulae (7) to (9) are also useful as an organic metal salt.

$$\left[\begin{array}{c} R^9 \\ \\ R^{10} \end{array} \underset{N}{\overset{S}{\bigcirc}} C-S \right]_{\!\!2} \!\!\!\!-Zn \qquad\qquad (7)$$

$$\left[\begin{array}{c} R^9 \\ \\ R^{10} \end{array} \underset{\substack{|| \\ C-N}}{\overset{O\ \ H}{\bigcirc}} \overset{S}{\bigcirc} \right]_{\!\!2} \!\!\!\!-Zn \qquad\qquad (8)$$

$$\left[\begin{array}{c} R^9 \\ \\ R^{10} \end{array} \underset{N}{\overset{N}{\bigcirc}} C-S \right]_{\!\!2} \!\!\!\!-Zn \qquad\qquad (9)$$
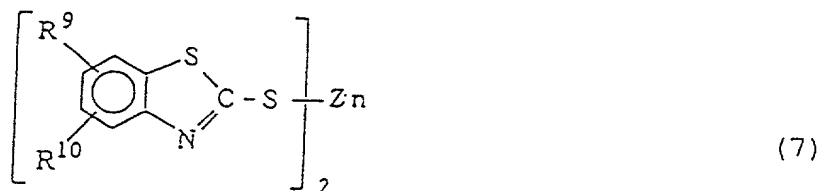
wherein R^9 and R^{10}, which may be the same or different, each represent a C_n ($n=1$ to 18) hydrocarbon group or a hydrogen atom.

In particular, zinc mercaptobenzothiazole of formula (7), zinc benzamidothiophenol of formula (8) and zinc mercaptobenzimidazole of formula (9), in which R^9 and R^{10} each represent a hydrogen atom, are suitably used.

Additionally, a zinc alkylxanthogenate represented by formula (10) is also useful as an organic metal salt.

$$\left[R^{11}-O-C-S \atop \overset{||}{S} \right]_{\!\!2} \!\!\!\!-Zn \qquad\qquad (10)$$
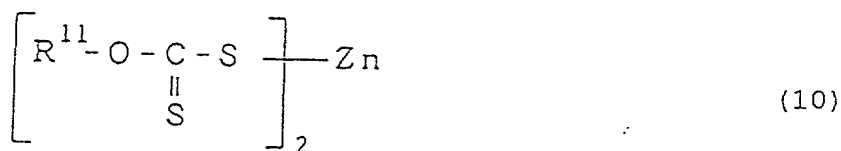
wherein R^{11} represents a C_n ($n=1$ to 18) hydrocarbon group.

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The organic metal salts represented by formulae (5) through (10) can be used either individually or as a mixture of two or more thereof. The species to be used in combination are not particularly limited.

The same action and effect as observed with the aforesaid organic metal salts can be obtained by using ADTC (such as a methylenebisdialkyldithiocarbamic acid) represented by formula (11):

$$\left[\begin{array}{c} R^{12} \\ \diagdown \\ N-C-S \\ \diagup \quad \| \\ R^{13} \quad S \end{array} \right]_2 CH_2 \tag{11}$$
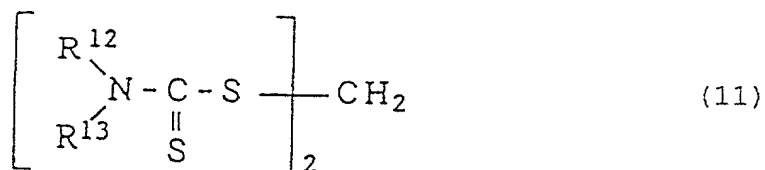
wherein R^{12} and R^{13}, which may be the same or different, each represent a C_n (n=1 to 18) hydrocarbon group.

(2) Amount of Reaction Film forming Agent Added

While the organic metal salt or ADTC has the effect of forming a reaction film in the small crevices to suppress progress of corrosion reaction as described above, sufficient effect is not manifested unless its content is higher than or equal to 0.1 wt%. It may be seen as unnecessary to define the upper limit of the content, but the compounds used as a reaction film forming agent are relatively expensive, and excessive addition of the reaction film forming agent may tend to accelerate reaction with the bearing material abnormally to induce corrosion or abnormal wear. Taking these respects into consideration, the content of the reaction film

forming agent is preferably limited to 10 wt% or less. In this particular mode of the invention, the amount of the reaction film forming agent to be added is set at 0.1 to 10 wt%. A still preferred range of the amount is 0.1 to 5 wt%.

(3) Hydrogen ion exponent pH

Even if the hydrogen ion exponent pH is in an acidic region of 7 or lower, early flaking of the bearing material can be prevented by incorporating the reaction film forming agent comprising the organic metal salt or ADTC into the lubricant. However, mere addition of the reaction film forming agent is insufficient. That is, with water in the lubricant, where a fresh small crevice is formed by the tensile stress, it is considered that the above-described corrosion reaction of hydrogen evolution type (chemical reaction formulae (1) to (4)) takes place near the inlet of the crevice immediately after the crevice formation. Such a corrosion reaction advances in competition with production of corrosion products. If the hydrogen ion concentration of the lubricant is high, that is, if the hydrogen ion exponent pH is low, the rate of production of corrosion products becomes high so that the reaction film is not sufficiently formed in the crevice, resulting in a failure to sufficiently suppress hydrogen absorption inside the bearing material. Accordingly, it is required to control the hydrogen ion concentration by addition of an alkaline pH adjustor. In this particular mode, the lower limit of the hydrogen ion exponent pH for assuring sufficient bearing reliability is set at 5.

On the other hand, even where a polyol ester oil, which exhibits the most excellent lubrication characteristics of the synthetic base oils, is used, if water seeps into the lubricant and the hydrogen ion exponent pH exceeds 13, there is a possibility that the base oil undergoes deterioration by hydrolysis. Accordingly, the upper limit of the hydrogen ion exponent pH is set at 13 in this mode so as to avoid such a drawback. For these reasons, the hydrogen ion exponent pH according to the second mode ranges from 5 to 13.

[Third Mode]

In the third mode for carrying out the invention, particles comprising an inorganic compound having an average particle size of 2 μm or smaller are incorporated into the lubricant in an amount of 0.001 to 3 wt% to improve oily film formation between the rolling surface and the raceway surface thereby to reduce the tangential force between the rolling surface and the raceway surface. Reduction in tangential force suppresses formation of small crevices to bring about improved durability of the rolling bearing.

Corrosion progress on bearing sites can be prevented effectively by not only suppressing the progress of the chemical reaction formula (2) according to the first mode but suppressing formation of crevices per se between non-metallic inclusions and the metallic matrix on the raceway surface.

Formation of the crevices can be suppressed by decreasing the tangential force between the rolling surface and the raceway surface, and the decrease of the tangential force can be achieved

by improving the oily film formation between the rolling surface and the raceway surface.

Where an oily film is formed and maintained sufficiently between the rolling surface and the raceway surface, it acts like a buffer producing a damping effect to lower the vibration level of resonance, etc. and the maximum load imposed on the rolling elements as is known from *NSK Technical Journal*, No. 656, p. 1 (1993) (hereinafter referred to as reference 7). Enhancement of such a damping effect of the lubricant decreases the tangential force between the rolling surface and the raceway surface thereby suppressing formation of small crevices.

The base oils, thickeners, and pH adjustors of the lubricant are the same as those used in the first and second modes. In what follows, the particles comprising an inorganic compound and the hydrogen ion exponent pH that characterize the third mode will be explained.

(1) Composition of Particles Comprising Inorganic Compound

The particles comprising an inorganic compound are uniformly dispersed in the lubricant. Even where the oily film receives a great shearing stress of high-speed rotation or becomes thinner due to rotation in high temperature, the particles present in the oily film serve to keep the oily film firm on the contact surface between the rolling surface and the raceway surface. Metal-to-metal contact is thus avoided to improve the seizure life of the bearing.

The particles comprising an inorganic compound enter the inside of a fibrous thickener to reinforce the gel structure.

Inorganic compounds which can be used include metal oxides such as SiO_2, Al_2O_3, MgO, TiO_2, PZT (available from Clevite, U.S.A.), and ZnO, metal hydroxides such as $Mg(OH)_2$, $Al(OH)_3$, and $Ca(OH)_2$, metal carbonates such as $MgCO_3$ and $CaCO_3$, and hydrates thereof; metal nitrides such as Si_3N_4, ZrN, CrN, and TiAlN; metal carbides such as SiC, TiC, and WC; (synthetic) clay minerals such as bentonite, smectite, and mica; and diamond. In addition, solid lubricants such as MoS_2, graphite, BN, and WS_2 can also be used.

To obtain improved affinity to the base oil or the thickener, inorganic compounds whose surface has been rendered lipophilic can be used for preference. Of the above-described inorganic compounds metal oxides and clay minerals which exhibit a thickening action by themselves are still preferred.

(2) Particle Size of Particles Comprising Inorganic Compound

Finer than the gel structure formed of a thickener, the particles of the inorganic compound can enter the inside of a fibrous thickener to reinforce the gel structure as mentioned above. As a result, the particles strengthen the lubricant's capability to form an oily film or enhance the damping effect of the lubricant thereby making a contribution to improvement in bearing life L. Therefore, the particle size is preferably as small as is consistent with the production cost. Particles whose average size is smaller than or equal to 1 μm would exhibit satisfactory seizure resistance.

Taking the seizure life into consideration, it is desirable that the particle size be smaller than the film of the base oil. As the film of the base oil used for rolling bearings is practically 0.2 μm or thinner, a preferred particle size is 0.2 μm or smaller.

If the average particle size is greater than 2 μm, such particles as act as foreign matter increase to accelerate wear of the rolling surface or the raceway surface, tending to cause early damage of the bearing or to deteriorate acoustic characteristics of the bearing. Hence in this mode of the invention the particle size of the inorganic compound is limited to 2 μm or smaller, preferably 0.2 μm or smaller, in terms of average particle size.

While it is preferred for the particles to have a nearly spherical shape, such polyhedral particles as cubic particles or hexahedral particles or needle-like particles can be used with no problem as long as their average particle size is not greater than 2 μm.

(3) Amount of Particles Comprising Inorganic Compound Added

As mentioned above, addition of particles comprising an inorganic compound to the lubricant contributes to improvement in bearing durability, but the effect as expected cannot be obtained sufficiently if the amount added is less than 0.001 wt%. If, on the other hand, the amount exceeds 3 wt%, the inorganic compound particles increase in number to accelerate wear, which adversely affects the seizure resistance. Accordingly, the amount of the particles comprising the inorganic compound is limited to 0.001 to

3 wt%, preferably 0.005 to 3 wt%.

(4) Hydrogen ion exponent pH

Addition of particles comprising an inorganic compound having an average particle size of 2 μm or smaller to the lubricant improves oily film formation, which is effective in preventing early flaking of a bearing material even if the hydrogen ion exponent pH is in an acidic range of 7 or lower. However, similarly to the second mode, mere addition of the particles is not enough. That is, with water in the lubricant, where a fresh small crevice is formed by the tensile stress, it is considered that the above-described corrosion reaction of hydrogen evolution type (chemical reaction formulae (1) to (4)) takes place near the inlet of the crevice immediately after the crevice formation. Such a corrosion reaction proceeds in competition with production of corrosion products. If the hydrogen ion concentration of the lubricant is high, that is, if the hydrogen ion exponent pH is low, the rate of production of corrosion products becomes high so that a strong reaction film is not sufficiently formed in the crevice, resulting in a failure to sufficiently suppress hydrogen absorption inside the bearing material. Accordingly, it is required to control the hydrogen ion concentration similarly to the second mode. In this particular mode, the lower limit of the hydrogen ion exponent pH for assuring sufficient bearing reliability is set at 5.

On the other hand, if water seeps into the lubricant to increase the hydrogen ion exponent pH over 13, there is a possibility

that the base oil undergoes deterioration by hydrolysis as described as to the second mode. Accordingly, the upper limit of the hydrogen ion exponent pH is set at 13 in this mode so as to avoid such a drawback. For these reasons, the hydrogen ion exponent pH according to the third mode ranges from 5 to 13.
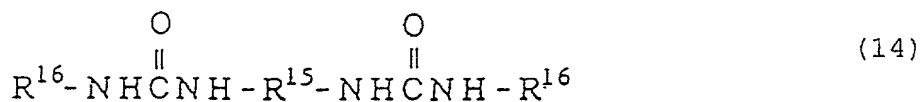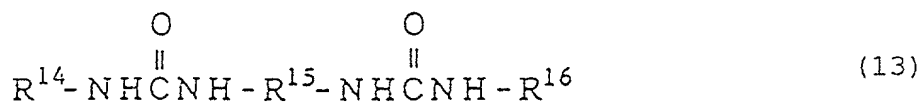
[Fourth Mode]

While the thickener used in the third mode is not particularly limited, addition of the inorganic compound to the lubricant can be replaced with use of a diurea compound containing an aromatic amine (hereinafter referred to as an aromatic diurea compound) or a mixture of the aromatic diurea compound and a diurea compound containing no aromatic amine (hereinafter referred to as a non-aromatic diurea compound) as a thickener in the fourth mode of the invention. By this mode oily film formation can be improved to provide a rolling bearing having a desired bearing life L.

As is apparent from reference 7 cited in regard to the third mode, it is known that an oily film sufficiently held between the rolling surface and the raceway surface shows a damping effect to reduce the level of vibrations of resonance, etc. and the maximum load imposed on the rolling elements. Further, the strength of the gel structure varies depending on the composition of the thickener used. Strengthening the gel structure would enhance the capability to form an oily film between the rolling surface and the raceway surface. It will follow that the oily film diminishes the tangential force between the raceway surface and the rolling surface

to hinder formation of crevices in the interface between the non-metallic inclusions and the metal matrix, thereby to improve the rolling fatigue strength of the rolling bearing.

Now a thickener comprising the aromatic diurea compound or a mixture of the aromatic diurea compound and the non-aromatic diurea compound makes the gel structure stronger to improve the rolling fatigue life.

Diurea compounds are obtainable by reacting a diisocyanate and a monoamine under prescribed conditions. The aromatic diurea compound is represented by formulae (12) or (13), and the non-aromatic diurea compound is represented by formula (14):

$$R^{14}\text{-}NHCNH\text{-}R^{15}\text{-}NHCNH\text{-}R^{14} \qquad (12)$$

$$R^{14}\text{-}NHCNH\text{-}R^{15}\text{-}NHCNH\text{-}R^{16} \qquad (13)$$

$$R^{16}\text{-}NHCNH\text{-}R^{15}\text{-}NHCNH\text{-}R^{16} \qquad (14)$$
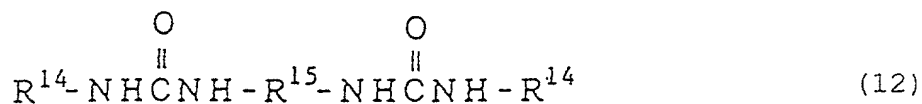
wherein R^{14} is an aromatic amine residue composed of a C_n (n=7 to 12) aromatic ring-containing hydrocarbon group, such as a toluoyl group, a xylyl group, a β-phenchyl group, a t-butylphenyl group, a dodecylphenyl group, a benzyl group or a methylbenzyl group; R^{16} is a non-aromatic amine residue, representing a cyclohexyl group, a C_n (n=7 to 12) alkylcyclohexyl group or a C_n (n=8 to 20) straight-chain alkyl group, such as a cyclohexyl group, a

methylcyclohexyl group, a dimethylcyclohexyl group, an ethylcyclohexyl group, a diethylcyclohexyl group, a propylcyclohexyl group, an isopropylcyclohexyl group, a 1-methyl-3-propylcyclohexyl group, a butylcyclohexyl group, a pentylcyclohexyl group, a pentylmethylcyclohexyl group, a hexylcyclohexyl group, an ethyl group, a butyl group or an octyl group, with a methylcyclohexyl group or an ethylcyclohexyl group being preferred; R^{15} is a diisocyanate residue composed of a divalent C_n (n=6 to 15) aromatic ring-containing hydrocarbon group, such as the groups represented by formulae (15) to (17):

(15)

(16)

(17)
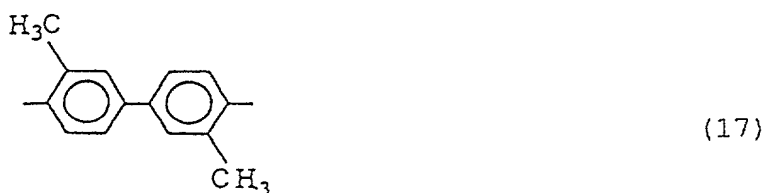
The aromatic amine residue R^{14} and the non-aromatic amine residue R^{16} are related in such a manner that an aromatic ring molar ratio Z, being defined by equation (I) shown below, ranges from 0.5 to 0.95.

Z = Number of moles of R^{14}/(number of moles

of R^{14} + number of moles of R^{16})　　　　... (I)

If the aromatic ring molar ratio Z is less than 0.5, the lubricant is liable to leak outside. That is, leakproofness of the lubricant is not secured. If the aromatic ring molar ratio Z exceeds 0.95, the flowability decreases to reduce seizure resistance. Accordingly, the aromatic ring molar ratio Z is adjusted within a range of from 0.5 to 0.95 in this mode, and the compounds represented by formulae (12) to (14) are mixed appropriately to prepare a thickening agent having that ratio.

Where the non-aromatic amine residue R^{16} is an alkylcyclohexyl group, the aromatic ring molar ratio Z is preferably 0.65 to 0.85. Where the non-aromatic amine residue R^{16} is a straight-chain alkyl group, the aromatic ring molar ratio Z is preferably 0.70 to 0.95.

If the thickener content in the lubricant is less than 8 wt%, the gelling ability is insufficient for obtaining sufficient hardness, and lubricant leakage increases. If the content exceeds 35 wt%, on the other hand, the durability under high temperature and high speed conditions is deteriorated noticeably. In this mode, accordingly, the thickener content in the lubricant is limited within a range of from 8 to 35 wt% and is preferably in a range of from 17 to 33 wt%.

To return to the formulae (12) to (14), the diurea compounds represented by formula (12) include, for example, compounds represented by structural formulae (18) and (19); the diurea

compounds represented by formula (13) include, for example, compounds represented by structural formulae (21) to (23); and the diurea compounds represented by formula (14) include, for example, compounds represented by structural formulae (24) to (27):

$$\text{H}_3\text{C}-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle(\text{CH}_3)-\text{NHCONH}-\langle\bigcirc\rangle(\text{CH}_3) \qquad \cdots (18)$$

$$\text{H}_3\text{C}-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle-\text{CH}_2-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle(\text{CH}_3) \qquad \cdots (19)$$

$$\text{H}_3\text{C}-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle(\text{CH}_3)-\text{NHCONH}-\langle\bigcirc\rangle \qquad \cdots (20)$$

$$\text{H}_3\text{C}-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle-\text{CH}_2-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle \qquad \cdots (21)$$

$$\text{H}_3\text{C}-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle(\text{CH}_3)-\text{NHCONH}-\text{C}_8\text{H}_{17} \qquad \cdots (22)$$

$$\text{H}_3\text{C}-\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle-\text{CH}_2-\langle\bigcirc\rangle-\text{NHCONH}-\text{C}_8\text{H}_{17} \qquad \cdots (23)$$

$$\langle\bigcirc\rangle-\text{NHCONH}-\langle\bigcirc\rangle(\text{CH}_3)-\text{NHCONH}-\langle\bigcirc\rangle \qquad \cdots (24)$$

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$$\langle H\rangle\text{-NHCONH-}\langle O\rangle\text{-CH}_2\text{-}\langle O\rangle\text{-NHCONH-}\langle H\rangle \quad \cdots (25)$$

$$C_8H_{17}\text{-NHCONH-}\langle O\rangle\text{-NHCONH-}C_8H_{17} \quad \cdots (26)$$
$$\overset{\displaystyle\quad\quad\quad\quad CH_3}{}$$

$$C_8H_{17}\text{-NHCONH-}\langle O\rangle\text{-CH}_2\text{-}\langle O\rangle\text{-NHCONH-}C_8H_{17} \quad \cdots (27)$$
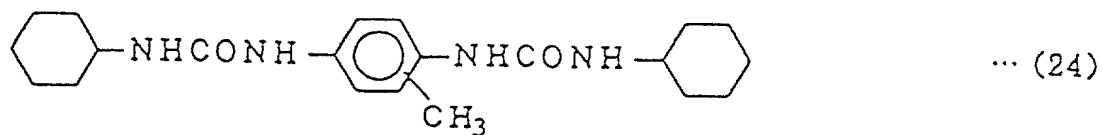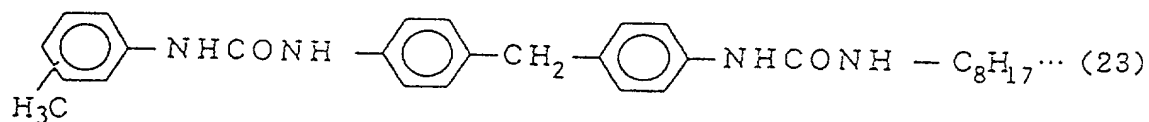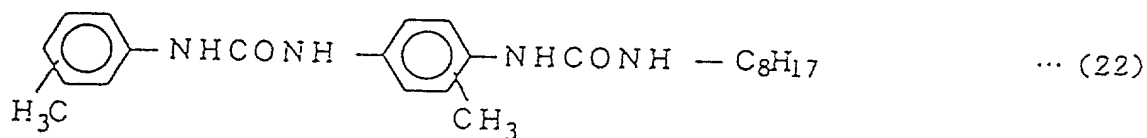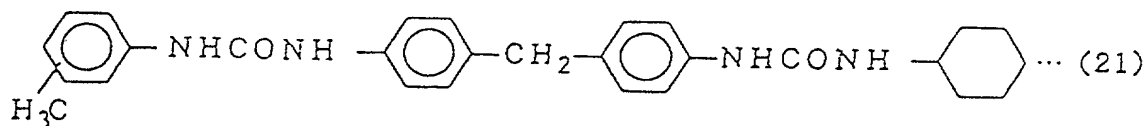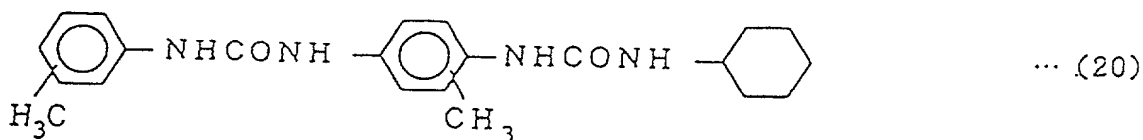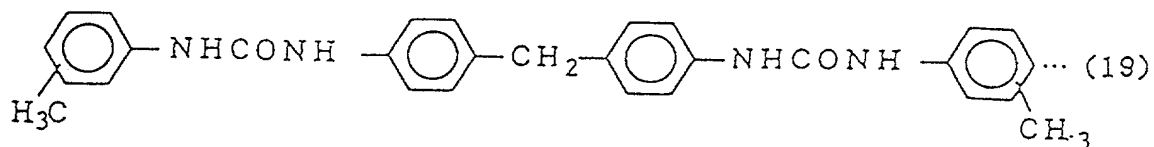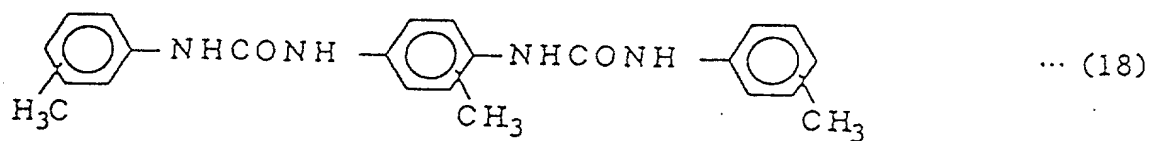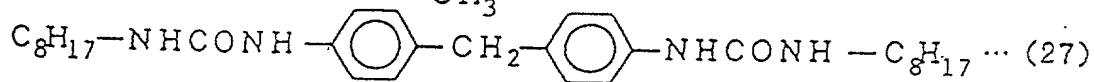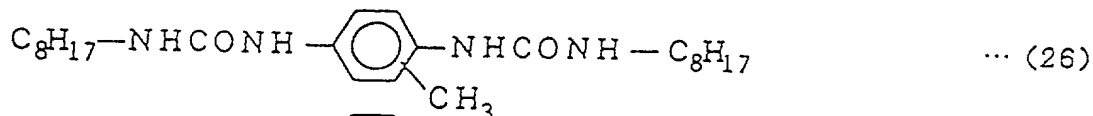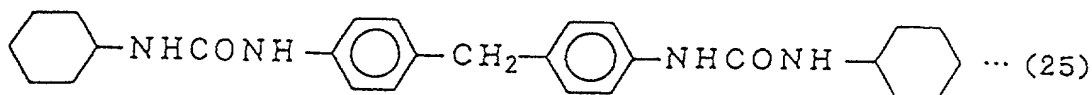
Examples of the present invention will now be given in detail.

[First Example]

The applicant prepared bearing parts, using high carbon chromium bearing steel species 2 (SUJ2) having been subjected to hardening and tempering (dipping hardening). The bearing parts were assembled into a deep groove ball bearing with a contact rubber seal. Grease having a varied hydrogen ion exponent pH was sealed into the annular space formed by the rolling elements and the races. The bearing was set on a test machine as a pulley side bearing of an automotive engine alternator to conduct a durability test. A plastic molded cage was used. The inner race was a rotating race, and the outer race was a fixed race.

The specifications of the bearing were as follows.

Bearing Specifications:

Designation: 6303 (reinforced)

Outer diameter D of outer race: 47 mm

Inner diameter d of inner race: 17 mm

Width (as assembled): 14 mm

Basic movement rated load C: 13500 N

Rockwell C hardness HRC

      Races: 62

      Rolling elements: 63

Retained austenite concentration γ_R

      Raceway surface of races: 10 vol%

      Rolling surface of rolling elements: 9 vol%

Retained austenite difference $\Delta\gamma_R$: +1 vol%

      The retained austenite difference $\Delta\gamma_R$ is obtained by subtracting the retained austenite concentration on the rolling surface of the rolling elements from that on the raceway surface of the races. Where there is a difference in retained austenite concentration between the inner race and the outer race, the higher concentration is used for calculation to obtain the difference $\Delta\gamma_R$.

      Table 1 shows the particulars of the grease subjected to the durability test and the results of the durability test.

TABLE 1

	Bearing No.	Thickener Kind[**]	Thickener Amount (wt%)	Base Oil Kind	Base Oil Dynamic Viscosity (mm²/sec. 40°C)	Worked Consistency (NLGI grade)	pH Adjustor Kind	pH Adjustor Amount (wt%)	pH of Grease	Water Concn. of Grease before Test (wt%)	Results of Durability Test				
E[*]	1	A	20	PAO	48	No. 2	OcA	5	9.1	0.11	good	good	good	good	good
	2	A	20	PAO	48	No. 2	StA	5	9.5	0.08	good	good	good	good	good
	3	B	15	PAO	48	No. 3	Na₂CO₃	3	8.0	0.15	good	good	good	good	good
	4	B	15	DAPE	100	No. 3	K₂CO₃	0.5	9.6	0.07	good	good	good	good	good
	5	A	20	DAPE	100	No. 2	StLi	7	7.0	0.09	good	good	good	good	good
	6	B	10	PAO	48	No. 2	StLi	12	9.9	0.12	good	good	good	good	good
	7	B	10	PAO	48	No. 2	NaOH	1	12.0	0.09	good	good	good	good	good
	8	B	10	PAO	48	No. 2	NaOH	2	13.0	0.09	good	good	good	good	good
C[*]	51	A	20	PAO	48	No. 2	-	0	5.4	0.10	bad (420hr)	bad (399hr)	bad (370hr)	bad (330hr)	bad (240hr)
	52	B	15	DAPE	100	No. 3	-	0	3.8	0.14	bad (389hr)	bad (254hr)	bad (208hr)	bad (184hr)	bad, 5hr
	53	B	15	DAPE	100	No. 3	OcA	0.01	5.7	0.08	good (560hr)	bad (451hr)	bad (390hr)	bad (321hr)	bad
	54	B	15	DAPE	100	No. 3	OcA	0.09	6.9	0.15	good	good	good	bad (709hr)	bad (650hr)

Note) * E: Example, C: Comparative Example

    ** Diurea compound A or B

Diurea compound A used as a thickener in Examples 1, 2 and 5 and Comparative Example 51 is a mixture of 4,4'-diphenylmethane diisocyanate (MDI) having a diphenylmethyl group as a diisocyanate residue R^2 and cyclohexylamine (CHA) having a cyclohexyl group as an amine residue R^1 and R^3 at a molar ratio of 1:2.

Diurea compound B used as a thickener in Examples 3, 4 and 6 to 8 and Comparative Examples 52 to 54 is a mixture of MDI, cyclohexylamine (CHA), and stearylamine (StA) at a molar ratio of 1:1:1. In the diurea compound B the diisocyanate residue R^2 is a diphenylmethyl group; the amine residue R^1 is a cyclohexyl group; and the amine residue R^3 is an octadodecyl group (i.e., a stearyl group).

As a base oil, a poly-α-olefin (PAO) having a dynamic viscosity of 48 mm²/sec at 40°C was used in Examples 1 to 3 and 6 to 8 and Comparative Example 51, and a dialkyldiphenyl ether (DAPE) having a dynamic viscosity of 100 mm²/sec at 40°C was used in Examples 4 and 5 and Comparative Examples 52 to 54.

While the method for preparing grease is not particularly limited, the grease used here was prepared as follows. A predetermined amount of MDI was added to the base oil, and the mixture was kept at a predetermined temperature required for reaction (70 to 80°C). Prescribed amounts of stearylamine (StA) and/or cyclohexylamine (CHA) were added thereto to cause reaction. The reaction mixture was heated up to 160°C while stirring and, at the same time, 0.5 wt% of a 2,6-di-t-butyl-p-cresol derivative was added thereto as an antioxidant, followed by allowing the mixture

to cool to about room temperature (about 20°C) while stirring. While the mixture was allowed to cool, 3 wt% of barium dinonylnaphthalenesulfonate having previously been dispersed or dissolved was added as a rust inhibitor, and a prescribed pH adjustor was added. Finally, the reaction product cooled to around room temperature was milled in a roll mill to prepare grease.

The pH adjustor used was octylamine (OcA) in Example 1 and Comparative Examples 53 and 54, stearylamine (StA) in Example 2, Na_2CO_3 in Example 3, potassium carbonate (K_2CO_3) in Example 4, lithium stearate (StLi) in Examples 5 and 6, and NaOH in Examples 7 and 8. Any pH adjustor was not used in Comparative Examples 51 and 52.

The hydrogen ion exponent pH was measured as follows. A solvent was compounded from toluene, 2-propanol, and water at a toluene:2-propanol:water volume ratio of 500:495:5. In 50 ml of the resulting solvent was dissolved 0.1 g of the grease prepared above at 25°C, and the hydrogen ion exponent pH of the solvent was measured with a pH meter. The measured value was taken as a hydrogen ion exponent pH of the grease.

The "worked consistency" in Table 1 is a value indicative of the softness of the grease. The mixing ratio of the base oil and the thickener was adjusted so that the grease might have a worked consistency of No. 2 (265 to 295) or No. 3 (220 to 250) according to NLGI grades, which is practical for closed bearings.

The conditions in the durability test were as follows.
[Durability Test]

Test load F: 1890 N

Average number of rotation (n) of rotating shaft: 8000 rpm

(2000 to 14000 rpm)

Lubricant: Characteristic grease

Amount of grease: 2.3 g

In the durability testing apparatus (not shown by drawing), the test load corresponded to the tension of a driving belt going through the pulley. That is, the tension of the driving belt was applied to the pulley. The applied load was received by the bearing on the pulley side and the bearing on the opposite side. The tension of the driving belt was adjusted so as to give a load of 1890 N (test load) to the bearing on the pulley side.

The rotating speed of the driving shaft was repeatedly varied between 2000 rpm and 14000 rpm, taking 30 seconds for speed up from 2000 to 14000 rpm and 30 seconds for slowdown from 14000 to 2000 rpm.

In this first example, although water was not added to the lubricant, the lubricant could have some water content even with no water's seeping in from the outside because the lubricant was to absorb moisture of the atmosphere. The water content of the lubricant before the durability test was found to be 0.08 to 0.15 wt% as shown in Table 1, measured by a Karl Fischer's method.

The durability test was undertaken on 5 bearings for each of Examples 1 to 8 and Comparative Examples 51 to 54. The running time of the first bearing to have underwent flaking was taken as a bearing life L, which was compared with the rated life L_{10} of the bearing to evaluate the durability of the bearing.

The term "rated bearing life L_{10}" denotes a calculated time corresponding to the total number of rotations until which 90%, in number, of bearings of the same size and lot continue rotating without undergoing flaking due to rolling fatigue. In the case of deep groove ball bearings, the rated bearing life L_{10} is obtained from basic movement rated load C (N), test load F (N), and number of rotation n (rpm) of the driving shaft according to equation (II):

$$L_{10} = (C/F)^3 \times 10^6/(60n) \qquad \ldots \text{(II)}$$

It is accepted that bearings produced by making use of the latest technology relating to material steel or working suffer from no flaking at all within the rated life L_{10} as long as a sufficient oily film is formed between the rolling surface of the rolling elements and the raceway surface of the races. Therefore, rolling bearings, even those having water in their lubricant, should satisfy at least the rated life L_{10} as a measure for evaluating durability. Where a bearing is used under such a situation that the bearing is greatly affected by the water content in the lubricant because of the influences of vibrations, etc. irrespective of whether or not water from the outside seeps in the lubricant, it occurs not infrequently that flaking takes place in a shorter time than the rated life L_{10}. It is therefore required in durability evaluation that the time at which flaking occurs be at least the rated life L_{10}. In this example, the basic movement rated load C being 135000 N, the test load F being 1890 N, and the average number of rotation

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n of the rotating shaft being 8000 rpm, equation (II) gives a rated life L_{10} of 759 hours. Whether or not the time until occurrence of flaking exceeds the rated life L_{10} can be a criterion.

As is apparent from Comparative Examples 51 to 54 in Table 1, in case where the grease is acidic, having a small hydrogen ion exponent pH, flaking of the bearing part is observed before the running time reaches the rated life L_{10}. As the hydrogen ion exponent pH rises, the flaking characteristics are improved. However, because the hydrogen ion exponent pH of the grease is lower than or equal to 6.9 in Comparative Examples 51 to 54, not all the test samples clear the rated life L_{10}, showing a failure to exhibit satisfactory durability.

In Examples 1 to 8, to the contrary, the hydrogen ion exponent pH falls within the range of from 7 to 13. It is seen that every test sample secures a bearing life L longer than or equal to the rated life L_{10}, proving to satisfy the durability requirement as expected.

The applicant further carried out another durability test on the samples of Example 7 and Comparative Examples 53 and 54 in the same manner as described above, except that the rolling elements were exchanged for those having a retained austenite concentration of 11 vol% so that the retained austenite difference $\Delta\gamma_R$ might be less than 0, with the other conditions being unchanged. As a result, all the five samples each of Examples 7' and Comparative Example 54', which correspond to Example 7 and Comparative Example 54, respectively, did not suffer from flaking even after the passage

of the rated life L_{10}. To the contrary, 3 out of 5 samples of Comparative Example 53', which corresponds to Comparative Example 53, did not suffer from flaking after the passage of the rated life L_{10}, but one of the remainder underwent flaking in 688 hours, and the another in 640 hours.

It is thus proved that a bearing life L exceeding the rated life L_{10} can be obtained in case where the retained austenite difference $\Delta\gamma_R$ is set below zero even with the hydrogen ion exponent pH being somewhat small, as compared with the case in which $\Delta\gamma_R$ is greater than or equal to zero.

[Second Example]

In a second example the applicant prepared several kinds of grease which contained an organic metal salt or ADTC and which had its hydrogen ion exponent pH adjusted with a pH adjustor, sealed the resulting grease into the inside of deep groove ball bearings, and undertook a durability test in the same manner as in the first example.

In the second example, grease was prepared as follows. A poly-α-olefin (PAO) having a dynamic viscosity of 48 mm^2/sec at 40°C was used as a base oil, to which 15 wt% of diurea compounds were added as a thickener. More specifically, MDI was added to the base oil PAO, and the resulting solution was kept at a temperature necessary for reaction (70 to 80°C). To the solution were added 1 mol of cyclohexylamine (CHA) and 1 mol of octadecylamine per mole of MDI to allow to react. Thereafter, the reaction mixture was heated up to a temperature of 160°C while stirring and, at the same

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time, 0.5 wt% of a 2,6-di-t-butyl-p-creosol derivative was added thereto as an antioxidant, followed by allowing to cool to about room temperature (about 20°C) with stirring. While the mixture was allowed to cool, 3 wt% of barium dinonylnaphthalenesulfonate having previously been dispersed or dissolved was added as a rust inhibitor, and a prescribed pH adjustor and a prescribed organic metal salt or ADTC were added. Finally, the reaction product cooled to around room temperature was milled in a roll mill to prepare grease.

The grease was compounded so as to have a worked consistency of No. 2 (265 to 295) according to NLGI grades, which is practical for closed bearings.

The specifications of test bearings, durability test conditions, and the method of hydrogen ion exponent pH measurement are the same as in the first example and are not described here.

Table 2 shows the particulars of the grease subjected to the durability test and the results of the durability test.

TABLE 2

	Bearing No.	pH Adjustor		Reaction Film Forming Agent		pH of Grease	Results of Durability Test				
		Kind	Amount (wt%)	Kind	Amount (wt%)						
Example	11	OcA	0.01	MoDTC	2.0	5.5	good	good	good	good	good
	12	StA	0.01	NiDTC	3.0	5.2	good	good	good	good	good
	13	StA	0.1	MoDTC/MoDTP	1/1	5.7	good	good	good	good	good
	14	StA	0.01	MoDTC/ZnDTP	1.5/1.5	5.3	good	good	good	good	good
	15	OcNa	0.05	SbDTC	1.0	5.4	good	good	good	good	good
	16	OcNa	0.05	BiDTC	3.0	5.5	good	good	good	good	good
	17	K$_2$CO$_3$	0.05	ADTC	1.0	5.3	good	good	good	good	good
Comparative Example	61	–	–	–	–	3.2	bad (355hr)	bad (233hr)	bad (285hr)	bad (166hr)	bad (104hr)
	62	–	–	TeDTC	1.0	3.3	good	good	medium	bad (721hr)	bad (688hr)

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The pH adjustor used was octylamine (OcA) in Example 11, stearylamine (StA) in Examples 12 to 14, sodium octanoate in Examples 15 and 16, and potassium carbonate (K_2CO_3) in Example 17. Any pH adjustor was not used in Comparative Examples 61 and 62.

In Examples 11 to 16 and Comparative Example 62, an organic metal salt was used as a reaction film forming agent. Specifically, a molybdenum dialkyldithiocarbamate (MoDTC) and a nickel dialkyldithiocarbamate (NiDTC) were used in Examples 11 and 12, respectively. MoDTC and a molybdenum dialkyldithiophosphate (MoDTP) were used in Example 13, and MoDTC and a zinc dialkyldithiophosphate (ZnDTP) were used in Example 14. In Example 15 was used an antimony dialkyldithiocarbamate (SbDTC), and a bismuth dialkyldithiocarbamate (BiDTC) was used in Example 16. A tellurium dialkyldithiocarbamate (TeDTC) was used in Comparative Example 62. ADTC was used in Example 17.

As is apparent from Table 2, in Comparative Example 61 wherein no reaction film forming agent was added, and the hydrogen ion exponent pH was as low as 3.2, none of the samples satisfied the rated life L_{10} (=759 hours) because of the failure to suppress the progress of the cathode reaction in the corrosion reaction of hydrogen evolution type. Flaking developed in some samples in an extremely short time. In Comparative Example 62 in which an organic metal salt was added, the durability was improved to some extent, but flaking developed in some samples within the rated life L_{10}. The sample rated "medium" in Comparative Example 62 was not greatly

damaged in the durability test, whereas examination after the testing revealed slight flaking.

Examples 11 to 17 show the cases in which the hydrogen ion exponent pH was adjusted at or above 5, ranging from 5.2 to 5.7, and 1.0 to 3.0 wt% of a reaction film forming agent (an organic metal salt or ADTC) was added. All the samples of these examples secured the bearing life L longer than or equal to the rated life L_{10}, proving durable as expected.

Then the applicant prepared grease having its hydrogen ion exponent pH adjusted to 5.1 to 5.3 by addition of 0.01 wt% of StA as a pH adjustor and containing TeDTC as a reaction film forming agent in a varied amount and examined the relationship between the amount of the reaction film forming agent and flaking of the bearing (bearing life L).

That is, grease having its hydrogen ion exponent pH adjusted to 5.1 to 5.3 and having a varied TeDTC content was prepared and sealed into the above-described deep groove ball bearings. The durability test was carried out on the thus prepared bearings to examine the relationship between the amount of the reaction film forming agent added and flaking of the bearings (bearing life L).

The relationship between TeDTC as a reaction film forming agent and flaking is shown in Fig. 1, in which 4 samples were examined for each grease. As is apparent from Fig. 1, the rated life L_{10} of the samples began to increase after the amount of addition exceeded 0.07 wt%. It is seen that amounts higher than and equal to 0.1 wt%

produce a sufficient effect on the bearing life L.

Further, grease containing 1 wt% of ZnDTC as an organic metal salt and having its hydrogen ion exponent pH varied by addition of a varied amount of OcA as a pH adjustor was prepared, and the relationship between the hydrogen ion exponent pH and flaking of the bearings (bearing life L) was examined. That is, grease containing the same kind and amount of a reaction film forming agent and having a varied hydrogen ion exponent pH was prepared and sealed into the above-described deep groove ball bearings. A durability test was carried out on the bearings to examine the relationship between the hydrogen ion exponent pH and flaking of the bearings (bearing life L).

Fig. 2 is a characteristics diagram showing the relationship of the hydrogen ion exponent pH of grease agent vs. flaking of bearings, in which 4 samples were examined for each grease. As is apparent from Fig. 2, half of the samples underwent flaking in a shorter time than the rated life L_{10} at a hydrogen ion exponent pH of 4 or lower. The bearing life L showed tendency toward improvement at a hydrogen ion exponent pH of about 4.4. Rolling bearings having a bearing life L exceeding the rated life $_{10}$ were obtained at a hydrogen ion exponent pH of 5.1 or higher.

[Third Example]

In the third example the applicant prepared several kinds of grease containing particles comprising an inorganic compound and having an average particle size smaller than or equal to 2 μm and

having its hydrogen ion exponent pH adjusted with a pH adjustor, and sealed the resulting grease in the inside of deep groove ball bearings to conduct a durability test in the same manner as in the first and second examples. The particulars of the grease subjected to the durability test and the results of the durability test are shown in Table 3.

TABLE 3

	Bearing No.	Thickener Kind**	Thickener Amount (wt%)	Base Oil Kind	Base Oil Dynamic Viscosity (mm²/sec. 40°C)	Worked Consistency (NLGI grade)	pH Adjustor Kind	pH Adjustor Amount (wt%)	pH of Grease	Inorganic Compound Kind	Inorganic Compound Particle size (μm)	Inorganic Compound Amount (wt%)	Results of Durability Test			
E	21	A	20	PAO	48	270	K₂CO₃	0.05	5.4	MgO	2.0	0.01	good	good	good	good
	22	A	20	DAPE	100	260	OcA	0.01	5.2	MgO	0.01	3.0	good	good	good	good
	23	B	15	DAPE	100	230	StNa	0.1	5.0	MgO	0.01	0.001	good	good	good	good
	24	B	17	PAO	48	220	OcNa	0.05	5.7	MgO	0.01	0.003	good	good	good	good
	25	A	17	PAO	48	283	StA	0.02	5.9	MgO	0.01	1.0	good	good	good	good
	26	B	13	DAPE	100	250	OcA	0.01	6.0	Al₂O₃	0.013	0.5	good	good	good	good
C*	71	B	15	DAPE	100	227	-	-	3.9	-	-	-	bad (184hr)	bad (208hr)	bad (254hr)	bad (389hr)
	72	A	20	PAO	48	273	K₂CO₃	0.02	4.5	MgO	2.0	0.01	bad (610hr)	bad (673hr)	good	good
	73	B	15	DAPE	100	230	StNa	0.05	4.4	MgO	0.01	0.001	bad (547hr,)	bad (681hr)	bad (703hr)	good

Note: * E: Example, C: Comparative Example

** Diurea compound A or B.

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In the third example, diurea compound A or diurea compound B was used as a thickener, and PAO or DAPE was used as a base oil similarly to the first example.

The base oil and the thickener were mixed to react, and the reaction mixture was heated to 160°C while stirring. An antioxidant was added thereto, followed by thoroughly stirring. While the mixture was allowed to cool, predetermined amounts of a rust inhibitor, a prescribed pH adjustor, and a metal oxide having an average particle size of 2 μm or smaller as an inorganic compound were added. After cooling to room temperature, the reaction product was milled in a roll mill to prepare grease.

As a pH adjustor was used K_2CO_3 in Example 21 and Comparative Example 72, OcA in Examples 22 and 26, StA in Example 25, sodium stearate (StNa) in Example 23 and Comparative Example 73, and sodium octanoate (OcNa) in Example 24, respectively. The metal oxide used as an inorganic compound was Al_2O_3 in Example 26 and MgO in other cases. The grease was compounded so as to have a worked consistency of No. 2 (265 to 295) or No. 3 (220 to 250) according to NLGI grades, which is practical for closed bearings.

The specifications of test bearings, durability test conditions, and the method of hydrogen ion exponent pH measurement are the same as in the first example and are not described here. Four test bearings were prepared for each grease.

As is apparent from Table 3, since in Comparative Example 71 no inorganic compound is added, and the hydrogen ion exponent

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pH is as low as 3.9, the cathode reaction (chemical reaction formula (2)) of hydrogen evolution type corrosion reaction is not inhibited from proceeding, and none of the samples satisfies the rated life L_{10} (=759 hours). Flaking occurred on a sample in an extremely short time. Comparative Examples 72 and 73 show somewhat improved durability owing to the MgO particles added, but not all the samples secured a bearing life L exceeding the rated life L_{10}.

To the contrary in Examples 21 to 26 in which the hydrogen ion exponent pH is adjusted between 5.2 and 6.0, i.e., 5 or more in every case, and 0.001 to 1.0 wt% of a metal oxide is added, all the samples have a bearing life longer than or equal to the rated life L_{10}, proving to satisfy the desired durability.

[Fourth Example]

In the fourth example the applicant prepared several kinds of grease containing, as a thickener, a diurea compound containing an aromatic amine and having its hydrogen ion exponent pH adjusted with a pH adjustor and sealed the resulting grease in the inside of deep groove ball bearings to carry out a durability test and a grease leak test.

The particulars of the grease prepared in the fourth example are shown in Table 4.

TABLE 4

Bearing No.	Thickener							Base Oil			Worked Consistency	pH Adjustor	
	Diisocyanate		Monoamine					Kind	Weight (g)	Dynamic Viscosity (mm²/sec. 40°C)		Kind	Amount (wt%)
	Kind	Weight (g)	R14 Component		R16 Component		Aromatic Ring Molar Ratio Z	Amount (wt%)						
			Kind	Weight (g)	Kind	Weight (g)								
31 E*	TDI	136	p-toluidine	133	CHA	31	0.80	30.0	DAPE	700	100	270	K₂CO₃	0.05
32	MDI	54	p-toluidine	37	CHA	9	0.80	10.0	DAPE / mineral oil	90 / 810	200	287	OcNa	0.05
33	MDI	109	p-toluidine	61	CHA	30	0.65	20.0	DAPE / PAO	400 / 400	70	256	OcA	0.01
34	TDI	69	aniline	46	CHA	35	0.55	15.0	PAO / polyol ester	765 / 85	400	274	StNa	0.1
35	MDI	200	p-toluidine	142	CHA	8	0.95	35.0	DAPE / PAO	260 / 390	50	206	NaOH	0.01
36	TDI	89	p-toluidine	104	OcA	7	0.95	20.0	PAO	800	100	295	StNa	0.1
37	TDI	90	p-toluidine	77	StA	83	0.70	25.0	DAPE / diester	675 / 75	80	280	K₂CO₃	0.05
38	MDI	129	p-toluidine	55	OcA	66	0.50	25.0	DAPE	750	100	290	StA	0.01
39	MDI	44	p-toluidine	24	CHA	12	0.65	8.0	PAO / polyol ester	460 / 460	200	308	OcA	1.0

TABLE 4 (continued)

Bearing No.		Thickener								Base Oil			Worked Consistency	pH Adjustor	
		Monoamine													
		Diisocyanate		R^{14} Component		R^{16} Component		Aromatic Ring Molar Ratio Z	Amount (wt%)	Kind	Weight (g)	Dynamic Viscosity (mm²/sec. 40°C)		Kind	Amount (wt%)
		Kind	Weight (g)	Kind	Weight (g)	Kind	Weight (g)								
E*	40	MDI	83	p-toluidine	28	CHA	39	0.40	15.0	DAPE	850	100	283	StNa	1.0
	41	TDI	71	p-toluidine	26	CcA	153	0.30	25.0	DAPE	750	100	300	K₂CO₃	0.2
C*	81	MDI	109	p-toluidine	61	CHA	30	0.65	20.0	DAPE	400	70	256	OcA	0.001
										PAO	400				
	82	TDI	89	p-toluidine	104	CcA	7	0.95	20.0	PAO	800	100	295	StNa	0.1

Note) * E: Example,   C: Comparative Example

In the fourth example, tolylene diisocyanate (TDI) or MDI in which the diisocyanate residue R^{15} is a tolyl group or a diphenylmethyl group, respectively, was used as a thickener. p-Toluidine or aniline having a tolyl group or a phenyl group, respectively, as an aromatic amine residue R^{14} was used as a R^{14} component, and cyclohexylamine (CHA), stearylamine (StA) or octylamine (OcA) having a cyclohexyl group or a straight-chain alkyl group as a non-aromatic residue R^{16} was used as a R^{16} component. DAPE, PAO, diester, polyol ester or mineral oil was used as a base oil.

TDI or MDI was added to the base oil, and the mixture was kept at a prescribed temperature (70 to 80°C). A predetermined amount of a compound compounded from the aromatic amine residue R^{14} and the non-aromatic amine residue R^{16} at a prescribed aromatic ring molar ratio Z was added thereto to react. The reaction mixture was heated to 160°C while stirring, and an antioxidant was added. The mixture was allowed to cool to about room temperature (about 20°C) with stirring. While the mixture was allowed to cool, a rust inhibitor and a prescribed pH adjustor were added. Finally, the reaction product cooled to around room temperature was milled in a roll mill to prepare grease.

As a pH adjustor, K_2CO_3, OcNa, OcA, StNa, NaOH or StA was used.

The grease was prepared by controlling the mixing ratio of the base oil and the thickener so as to have a worked consistency of about 200 to 300.

The hydrogen ion exponent pH of the grease was measured.
Then the grease was sealed into the inside of deep groove ball
bearings to conduct a durability test and a grease leak test. In
Table 5 are shown the hydrogen ion exponent pH of the grease and
the results of the durability test and the grease leak test.

TABLE 5

	Bearing No.	pH of Grease	Results of Durability Test				Results of Grease Leak Test (wt%)			
Example	31	5.2	good	good	good	good	1.5	1.9	2.1	2.6
	32	5.4	good	good	good	good	5.8	7.1	7.9	8.3
	33	5.7	good	good	good	good	2.8	3.3	3.7	4.1
	34	5.1	good	good	good	good	3.6	4.0	5.0	5.2
	35	5.9	good	good	good	good	1.2	1.4	1.9	2.0
	36	5.8	good	good	good	good	1.9	2.2	2.5	2.5
	37	5.5	good	good	good	good	1.8	1.8	2.3	2.4
	38	5.3	good	good	good	good	2.0	2.2	2.4	2.7
	39	8.0	good	good	good	good	6.8	7.3	8.5	9.6
	40	7.3	good	good	good	good	5.8	6.9	8.7	12.3*
	41	7.1	good	good	good	good	5.4	7.6	9.2	10.1*
Comparative Example	81	4.2	good	good	bad (705hr)	bad (599hr)	2.5	2.9	4.2	4.5
	82	4.8	good	good	good	bad (691hr)	2.0	2.3	2.7	2.8

The method for measuring the hydrogen ion exponent pH, the specifications of the test bearings, and the conditions of the durability test were the same as in the first to third examples. Four samples were prepared for each grease.

As is apparent from Table 5, in Comparative Examples 81 and 82 in which a diurea compound containing an aromatic amine is added as a thickener to the lubricant, some of the samples satisfy the rated life L_{10}. However, because the hydrogen ion exponent pH is as low as 4.2 or 4.8, not all the samples secured a bearing life L exceeding the rated life L_{10}.

In Examples 31 to 41, wherein a diurea compound containing an aromatic amine is added to the lubricant as a thickener and also the hydrogen ion exponent pH is adjusted to or above 5, i.e., between 5.1 and 8.0, all the samples tested secured a bearing life L longer than or equal to the rated life L_{10}, proving to satisfy the desired durability.

The grease leak test is explained below.

The grease leak test was carried out on contact rubber-sealed deep groove ball bearings with the grease sealed in under the following conditions. The amount of the grease having leaked by the end of the test was measured. The samples having a grease leak less than 10 wt% of the initial sealed amount of the grease were judged "pass". Four samples were tested for each grease.

[Grease Leak Test]

Bearing Spec.:   Designation 6301 (deep groove ball bearing)

Outer diameter D of outer race: 37 mm

Inner diameter d of inner race: 12 mm

Width (as assembled): 12 mm

Amount of Grease (initially sealed): 1.6 g

Speed of rotation of outer race: 14000 rpm

Inner race temperature: 160°C

Radial load: 141 kgf

Running time: 20 hrs

As is apparent from Table 5, although Examples 40 and 41 show satisfactory results with regard to their bearing life L owing to the hydrogen ion exponent pH adjusted to 5 or higher, the grease softens at the high temperature on account of the aromatic ring molar ratio Z as low as 0.30 or 0.40, the leakage of the grease exceeding 10 wt%.

To the contrary, no grease leak was observed in Examples 31 to 39 and Comparative Examples 81 and 82, in which the aromatic ring molar ratio Z is 0.5 or higher. It is thus proved that Examples 31 to 39 provide rolling bearings excellent in both bearing life L and grease leakproofness.

In Fig. 3 is shown the characteristic diagram illustrating the relationship between the amount (wt%) of the diurea compound added and the aromatic ring molar ratio Z. If the amount is less than 8 wt%, there is a possibility that the grease may leak at high temperature because the gelling ability is insufficient for obtaining sufficient hardness. If the amount exceeds 35 wt%, the

durability under high temperature and high speed conditions may be deteriorated. Where the aromatic ring molar ratio Z is less than 0.5, the grease is apt to leak outside, tending to fail to obtain sufficient leakproofness. Where the aromatic ring molar ratio Z exceeds 0.95, the grease reduces the flowability, tending to suffer from seizure damage in the early stage. Accordingly, it is preferable that the diurea compounds to be added be in area A in which the amount ranges from 8 to 35 wt%, and the aromatic ring molar ratio Z ranges from 0.5 to 0.95. It is also seen from the results in Table 4 that, where cyclohexylamine (CHA) is used as a R^{16} component, area B is preferred, in which the aromatic ring molar ratio Z ranges from 0.65 to 0.85; where a R^{16} component having a straight-chain alkyl group, such as stearylamine (StA) or octylamine (OcA), is used, the aromatic ring molar ratio Z is preferably in area B, ranging from 0.70 to 0.95. A still preferred range of the amount of the diurea compound is from 17 to 33 wt%.

Industrial Applicability

As described above in detail, the rolling bearing according to the present invention comprises outer and inner races and rolling elements which are rotatably put in between the outer and inner races with a lubricant sealed into the annular space formed by the rolling elements and the races, wherein the hydrogen ion exponent pH of the lubricant is adjusted in a range of from 7 to 13. The bearing can be protected against flaking on the bearing sites and exhibits improved durability even if it is used in the electric parts and

accessaries of an automobile engine where water tends to seep into the lubricant or where the bearing is easily affected by the water content of the lubricant by the action of vibrations.

Similar effects can be obtained by adding to the lubricant a prescribed amount of an organic metal salt or ADTC or an inorganic compound having an average particle size of 2 μm or smaller and adjusting the hydrogen ion exponent pH of the lubricant in a range of from 5 to 13. Similar effects can also be obtained when a diurea compound containing an aromatic amine is added to the lubricant as a thickener, with the hydrogen ion exponent pH being in the range of from 5 to 13.